IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Norihiko KAGA.

Serial No. : 10/080,669

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For : ELECTROCONDUCTIVE ENDLESS-BELT AND IMAGE FORMATION APPARATUS

Art Unit & Examiner : 1711, TRAN,THAO T

DECLARATION UNDER 37 CFR 1.132

ASSISTANT COMMISSIONER FOR PATENTS

WASHINGTON, D.C. 20231

Sir:

I, Norihiko KAGA, residing 3-5-5, Ogawahigashi-cho, Kodaira-shi, Tokyo, Japan declare that;

1. I graduated from Tokyo Institute of Technology with a Master's degree in Graduate School of Science and Engineering in March 1995, and joined BRIDGESTONE CORPORATION in April 1995. Then, I was engaged in the Research and Development division up to the present.

2. I am inventor of present U.S. Patent Application as identified above and familiar with the subject matter disclosed in the application.

3. Experiment

Object of Experiment

In order to make sure the Tg of the flexible component in the resin used in Examples 1 and 2 of the present invention, we would like to submit a Declaration

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enclosed herewith.

Resin Used for Measurement of Tg;

(1) Acrylonitrile-Butadiene-Styrene Resin Used in Example 1.

 (Produced by Daicel Polymer Ltd. Cevian V 510, Content of Butadiene;
10 mass %)

(2)   Polymer alloy (Produced by Daicel Polymer Ltd. Novalloy B 1700,
Content of Butadiene; 15 mass %) of Acrylonitrile-Butadiene-Styrene
Resin Used in Example 2 and Thermoplastic Polybutylene Terephthalate
Resin

Procedure of the Experiment

       Tmg (Tg) was measured using Power-compensation DSC apparatus.
Detailed method for the measurement was based on JIS K 7121-1987
"Testing Methods for Transition Temperatures of Plastics" enclosed
herewith.

Result of Measurement;

Glass transition temperature of the flexible component, butadiene
rubber, used in Example 1   Tmg = —81.6°C.
Glass transition temperature of the flexible component, butadiene
rubber, used in Example 2   Tmg = —84.5°C.
As shown in the above, the glass transition temperature Tmg (Tg) of the
resin (flexible component) was confirmed to be lower than 25°C.
DSC chart obtained in the above measurement is attached herewith.

4. I declare further that all statements made herein of my own
knowledge are true and that all statements made on information and
belief are believed to be true; and further that these statements were

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made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.
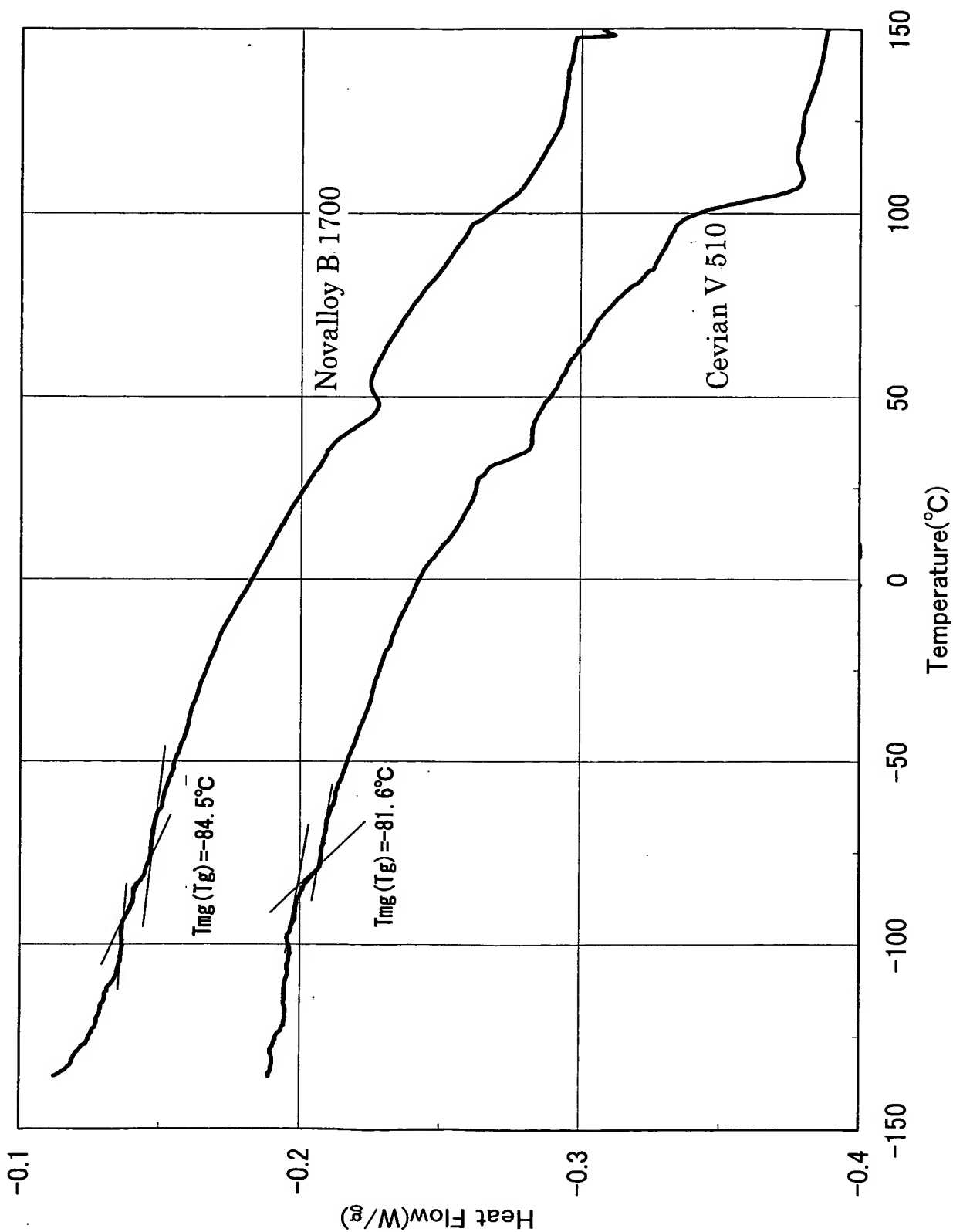
7 / July / 2005   Norihiko Kaga

Date   Norihiko   KAGA

DSC

Operator: kaga
Run Date: 15-jun-05 16:04

Novalloy B 1700

Cevian V 510

Tmg(Tg)=-84.5℃

Tmg(Tg)=-81.6℃

Heat Flow(W/g)

Temperature(℃)

JIS

JAPANESE INDUSTRIAL STANDARD

Testing Methods for Transition Temperatures of Plastics

JIS K 7121-1987

Translated and Published

by

Japanese Standards Association

In the event of any doubt arising,
the original Standard in Japanese is to be final authority

JAPANESE INDUSTRIAL STANDARD   J I S

Testing Methods for Transition   K 7121-1987
Temperatures of Plastics   (Reaffirmed: 1994)

1. Scope

This Japanese Industrial Standard specifies the testing methods for transition temperatures (melting temperatures, crystallization temperatures, and glass transition temperatures) of plastics.

Remark: These methods may also be applied to the crystal-crystal transition temperatures of plastics and various transition temperatures of plastics which form liquid crystal, as appropriate.

2. Definitions

The definitions of the main terms used in this Standard shall be as follows except as specified in JIS K 6900.

(1) **differential thermal analysis (DTA)** A method of measuring the difference in temperature between the test specimen and the reference substance as a function of temperature while varying the temperatures of the test specimen and the reference substance according to a controlled programme.

In this case, the reference substance consists of a vacant receptacle or a receptacle charged with α-alumina.

(2) **DTA curve** A curve drawn in differential thermal analysis by taking the temperature difference on the axis of ordinate and the temperature or time on the axis of abscissa.

(3) **differential scanning calorimetry (DSC)** The general term for the following two measuring methods:

(a) **power compensation differential scanning calorimetry (power-compensation DSC)** A method of measuring the difference in the input of thermal energy per unit time applied to the test specimen and the reference substance as a function of temperature so as to equalize their temperatures while varying their temperatures according to a controlled programme.

Applicable Standards:

JIS K 6900-Glossary of Terms Used in Plastic Industry

JIS K 7100-Standard Atmospheres for Conditioning and Testing of Plastics

JIS Z 8401-Rules for Rounding off of Numerical Values

Corresponding International Standard:

ISO 3146-Plastics-Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers

Reference Standard:

ASTM D 3418-82-Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis

(b) **heat flux differential scanning calorimetry (heat flux DSC)** A method of measuring the difference in temperature between the test specimen and the reference substance as a function of temperature while varying their temperatures according to a controlled programme.

In this measurement, the difference in temperature between the test specimen and the reference substance is proportional to the difference in the input of thermal energy per unit time.

(4) **DSC curve** A curve drawn in differential scanning calorimetry by taking on the axis of ordinate the difference in the input of thermal energy per unit time applied to the test specimen and the reference substance so as to equalize their temperatures and taking the temperature or time on the axis of abscissa.

(5) **base line** The part of a DTA curve or DSC curve in the temperature region where no transition nor reaction occurs in the test specimen.

Remark: In general cases, the curvature of the base line is equal to that of the DTA curve or DSC curve obtained when measuring with the vacant receptacle placed. In some cases, the curve can be regarded as a straight line in a narrow temperature region.

(6) **peak** In a DTA curve or DSC curve, the part where the curve leaves the base line and then returns to the same base line.

(7) **stepped change** In a DTA curve or DSC curve, the part where the curve leaves the former base line and shifts to a new base line.

Remark: A DTA curve or DSC curve in the part where a transition or reaction is taking place shows a form containing a peak, staged change, and their combinations.

(8) **peak height** The distance measured vertically to the axis of abscissa between an interposed base line and the peak crest.

3. Conditioning of Test Specimen

The conditioning methods for test specimens shall be classified into the following three kinds according to the measuring methods.

(1) **For Measurement of Transition Temperatures by Conditioning under Standard Atmospheric Conditions** The test specimen shall, as a rule, be conditioned before testing under the standard temperature condition grade 2 and the standard humidity condition grade 2 (temperature, $23 \pm 2°C$; relative humidity, 50 ± 5 %) specified in JIS K 7100 for 24 hours or longer. However, conditioning may be made by the method agreed upon between the parties concerned.

(2) **For Measurement of Melting Temperature after a Definite Heat Treatment** After the conditioning of (1), the test specimen shall be melted by heating to a temperature about 30°C higher than that at the end of the melting peak in the receptacle of DSC or DTA apparatus and after being maintained at the same temperature for 10 minutes, cooled to a temperature about 50°C lower than that at the appearing transition peak at a cooling rate of 5°C or 10°C per minute (refer to 8.6).

(3) **For Measurement of Glass Transition Temperature after a Definite Heat Treatment**   After the conditioning of (1), the test specimen shall be heated to a temperature at least about 30°C higher than that at the end of glass transition for non-crystalline products, and to a temperature at least about 30°C higher than that at the end of the melting peak for crystalline products in the receptacle of DSC or DTA apparatus, and after being maintained at the above respective temperatures for 10 minutes, rapidly cooled to a temperature about 50°C lower than the glass transition temperature (refer to 8.6).

4.   Testing Method

Tests shall be performed by either one of the following methods:

4.1 Differential thermal analysis (DTA)

4.2 Differential scanning calorimetry (DSC).

(1)   Power-compensation differential scanning calorimetry (power-compensation DSC)

(2)   Heat flux differential scanning calorimetry (heat flux DSC)

5.   Apparatus and Appliances

5.1 **DTA or DSC Apparatus**   The apparatus shall have two receptacle holders of equal heat capacity with a construction capable of being heated and cooled under the same heat exchange conditions. The power-compensation DSC apparatus shall be constructed so as to allow the measurement of the difference in thermal energy per unit time applied to the test specimen and the reference substance so as to equalize their temperatures. The heat flux DSC apparatus shall be so constructed that the difference in temperature between the test specimen and the reference substance is proportional to the difference in thermal energy input per unit time.

(1)   **Heating Rate**   The heating device shall be able to raise the temperature at the rates of 10°C and 20°C per minute with an accuracy of within ± 0.5°C per minute.

(2)   **Cooling Rate**   The cooling device shall be capable of lowering the temperature at a rate of 5°C or 10°C per minute.

(3)   **Gas Inflow Device**   The gas inflow device shall have a construction capable of making the inflowing gas flow around the test specimen.

(4)   **Receptacle**   The receptacle shall be made of a material having no risk of corrosion by the test specimen and having a high thermal conductivity.

(5)   **Recording Device**   The recording device shall be capable of automatic recording of the DTA curve or DSC curve.

(6)   **Noise Level**   The noise level shall be within 1/10 of the peak height or the height of the staged change.

5.2 <u>Appliances</u>   The appliances shall be as follows:

(1) <u>Gas Flowmeter</u>   The gas flowmeter shall be capable of measuring a range of 10 to 50 ml/min.

(2) <u>Chemical Balance</u>   The chemical balance shall have a reciprocal sensibility of 0.1 mg or higher.

6. Test Specimen

For the test specimen, a specimen within 0.5 mm in diameter or in each side length shall be used as it stands as the test specimen. A specimen exceeding 0.5 mm in size shall be cut into a test specimen of 0.5 mm or smaller in size. A sheet or film within 0.5 mm in thickness shall be cut into a size allowable in the receptacle without difficulty. Products which can be cut into thin pieces, such as a formed product or pellets shall be cut into a thickness of within 0.5 mm and further be cut into a size allowable in the receptacle without difficulty.

7. Temperature Calibration

The temperature calibration shall be performed based on a pure substance of 99.99 % or higher purity as shown in Table or the standard substance GM-754, 757, or 758 specified by the International Confederation for Thermal Analysis (ICTA) - National Bureau of Standards (NBS) by using the same gas flow rate and heating rate as in the actual test. The temperature scale shall be calibrated by the interpolation method by using the extrapolated onset temperature of transition of two or more kinds of pure substances or standard substances having temperatures close to the temperature to be determined. Pure substances shall be used after being freed from the surface oxide layer. Where an aluminium receptacle and zinc as the pure substance are used, only the value indicated for the first stage of heating for raising the temperature shall be used to avoid the risk of alloying at the time of melting.

Table.   Melting Points of Pure Substances

Name of pure substance	Melting point °C
Indium	156.4
Tin	231.9
Lead	327.4
Zinc	419.5

8. Procedure

The following procedures shall be carried out:

8.1 <u>Mass of Test Specimen</u>   Measure the mass of the test specimen to the nearest 0.1 mg by a chemical balance by taking about 5 mg in the measurement of melting and crystallization temperatures and about 10 mg in the measurement of glass transition temperature.

Where the test specimen contains a large amount of filler, take a quantity so as to make that of the plastic material 5 to 10 mg.

8.2 <u>Packing of Test Specimen in Receptacle</u>   The packing shall be performed as follows:

(1) Where the diameter or side lengths of the test specimen are within 0.5 mm, place it flatly and uniformly in the receptacle, and put on the receptacle cover and fix it. At this time, if the receptacle bottom is not flat, push the central part of the cover to flatten the bottom.

(2) Where the test specimen is in the form of a sheet or film, lay the required quantity to fill the receptacle, and put on the receptacle cover and fix it. At this time, if the receptacle bottom is not flat, push the central part of the cover to flatten the bottom.

(3) For a thinly-cut test specimen of a size matching the receptacle, pack it by the same method as in the case of a sheet and film.

Where the test specimen is small relative to the receptacle, lay and spread it flatly to leave no vacant space.

Remark: These procedures are important for improving the thermal contact between the test specimens, between the test specimen and receptacle, and between the receptacle and receptacle holder.

8.3 <u>Mounting of Receptacle</u>   Mounting of receptacle shall be performed as follows:

Mount the receptacle filled with the test specimens on one of the receptacle holders. Mount a receptacle with fixed cover on the other receptacle holder. However, where a large amount of test specimens is required, α-alumina powder may be packed in one of the receptacles in the same apparent volume as that of the test specimen.

8.4 <u>Flow Rate of Nitrogen</u>   Set the flow rate of nitrogen gas to a suitable value in the range of 10 to 50 ml/min, and continue inflow without changing the flow rate until the end of the test.

8.5 <u>Adjustment of Sensitivity</u>   Adjust the sensitivity so that the entire range of the DTA or DSC curve is drawn and in the case of measuring the melting and crystallization temperatures, the peak height becomes 25 % or more of the full scale of the recording paper sheet.

In the case of measuring the glass transition temperature, make adjustment so that the difference in vertical height on the stepped change curve becomes at least 10 % or more of the full scale of the recording paper sheet.

8.6 <u>Measurement of DTA or DSC Curve</u>   The measurement shall be performed as follows:

(1) Where the melting temperature is to be determined, preliminarily maintain the apparatus until it stabilizes at a temperature about 100°C lower than the melting temperature, and then heat to a temperature about 30°C higher than that at the end of melting peak at a heating rate of 10°C per minute to obtain a DTA or DSC curve.

Where the melting temperature is to be determined after the conditioning of 3. (2), stabilize the apparatus directly after conditioning, and then heat to a temperature about 30°C higher than that at the end of melting peak at a heating rate of 10°C per minute to obtain a DTA or DSC curve.

(2) Where the crystallization temperature is to be determined, heat to a temperature about 30°C higher than that at the end of melting peak in the procedure of (1), and after maintaining this temperature for 10 minutes, cool to a temperature about 50°C lower than that at the end of crystallization peak at a cooling rate of 5°C or 10°C per minute to obtain a DTA or DSC curve.

In this test, where crystallization progresses slowly and the base line on the low temperature side of the crystallization peak is difficult to decide, the test may be discontinued.

(3) Where the glass transition temperature is to be determined, preliminarily maintain the apparatus until it stabilizes at a temperature about 50°C lower than the transition temperature, and then heat to a temperature about 30°C higher than that at the end of transition at a heating rate of 20°C per minute to obtain a DTA or DSC curve.

Where the glass transition temperature is to be determined after the conditioning of 3.(3), perform the above procedure directly after conditioning.

9. Method of Reading DTA or DSC Curve

The DTA or DSC curve shall be read by the following procedures:

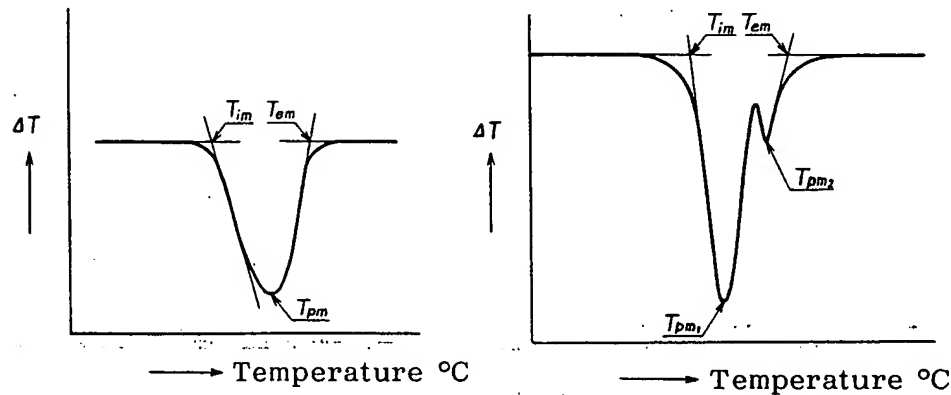### 9.1 Determination of Melting Temperatures (refer to Fig. 1) The determination shall be as follows:

(1) Find the melting peak temperature (T_{pm}) as the crest of the melting peak.

(2) Find the extrapolated onset temperature of melting (T_{im}) as the temperature at the intersection of the straight line formed by extending the base line on the low temperature side to the high temperature side and the tangent line drawn to the curve on the low temperature side of the melting peak at the point of maximum gradient.

(3) Find the extrapolated end temperature of melting (T_{em}) as the temperature at the intersection of the straight line formed by extending the base line on the high temperature side to the low temperature side and the tangent line drawn to the curve on the high temperature side of the melting peak at the point of maximum gradient. Where two or more melting peaks appears independently, find T_{pm} , T_{im} , and T_{em} for the respective peaks. Where two or more peaks are present in successive stages, find T_{im} , plural T_{pm} , and T_{em} .

Where melting progresses slowly and the base line on the low temperature side of the melting peak is difficult to decide, T_{im} may be left undermined.

Fig. 1. Example of Determination Method for Melting Temperatures

Where One Peak Is Present

Where Two or More Peaks Are
Present in Successive Stages

ΔT

T_{im} T_{em}

T_{pm}

⟶ Temperature °C

ΔT

T_{im} T_{em}

T_{pm_2}

T_{pm_1}

⟶ Temperature °C

9.2 Determination of Crystallization Temperatures (refer to Fig. 2)   The
determination shall be obtained according to the following:

(1) Find the crystallization peak temperature (T_{pc}) as the temperature at
the crest of the crystallization peak.

(2) Find the extrapolated onset temperature of crystallization (T_{ic}) as the
temperature at the intersection of the straight line formed by extend-
ing the base line on the high temperature side to the low temperature
side and the tangent line drawn to the curve on the high temperature
side of the crystallization peak at the point of maximum gradient.

(3) Find the extrapolated end temperature of crystallization (T_{ec}) as the
temperature at the intersection of the straight line formed by extend-
ing the base line on the low temperature side to the high temperature
side and the tangent line drawn to the curve on the low temperature
side of the crystallization peak at the point of maximum gradient.

Where two or more crystallization peaks appear independently, obtains
T_{pc} , T_{ic} , and T_{ec} for the respective peaks.

Where two or more peaks are present in successive stages, find T_{ic} ,
plural T_{pc} , and T_{ec} .

Where crystallization progresses slowly and the base line on the low
temperature side of the crystallization peak is difficult to decide, T_{ec}
may be left undermined.

Fig. 2. Example of Determination Method for Crystallization Temperatures

Where One Peak Is Present

Where Two or More Peaks Are
Present in Successive Stages
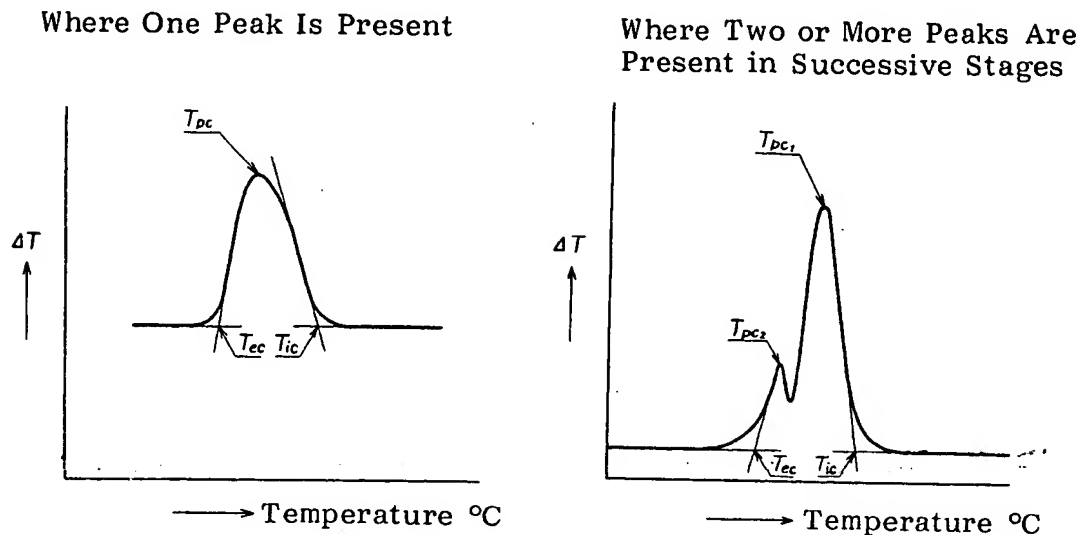
9.3 Determination of Glass Transition Temperatures (refer to Fig. 3) The determination shall be performed as follows:

(1) Find the mid-point temperature of glass transition (T_{mg}) as the temperature at the intersection of the straight line equidistant in the vertical axial direction from the straight lines formed by extending the respective base lines and the curve showing a stepped change of glass transition.

(2) Find the extrapolated onset temperature of glass transition (T_{ig}) as the temperature at the intersection of the straight line formed by extending the base line on the low temperature side to the high temperature side and the tangent line drawn to the curve showing a stepped change of glass transition at a point of maximum gradient.

(3) Find the extrapolated end temperature of glass transition (T_{eg}) as the temperature at the intersection of the straight line formed by extending the base line on the high temperature side to the low temperature side and the tangent line drawn to the curve showing a stepped change of glass transition at a point of maximum gradient.

Find the extrapolated end temperature of glass transition (T_{eg}) in the case in which a peak appears on the high temperature side of the stepped change as the temperature at the intersection of the straight line formed by extending the base line on the high temperature side to the low temperature side and the tangent line drawn to the curve on the high temperature side of the peak at the point of maximum gradient.

Fig. 3.   Example of Determination Method for
Glass Transition Temperatures

In the Case of Stepped Change   Where Peak Appears on High Tempera-
ture Side of Stepped Change

—→ Temperature °C   —→ Temperature °C
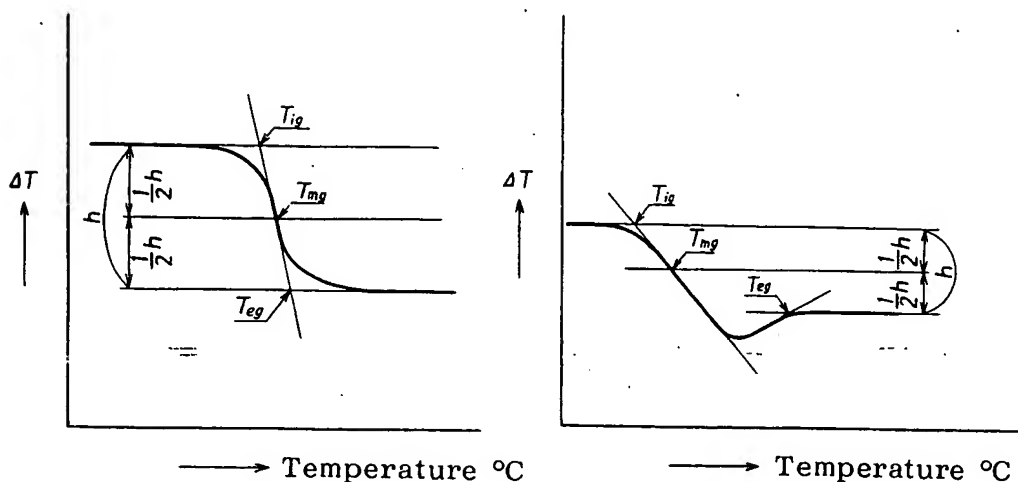
10. Method of Rounding Numerical Values

Temperature values shall be obtained to the first decimal place and rounded according to the method specified in JIS Z 8401.

11. Report

The following items shall be written in the report as required.

(1) Kind of material tested

(2) Manufacturer's name and type of test apparatus

(3) Shape, size, and mass of test specimen

(4) Conditioning of test specimen

(5) Inflow speed of nitrogen gas

(6) Heating rate, cooling rate, and temperatures at start and end of measurement

(7) Pure substance or standard substance used for temperature calibration

(8) Melting temperatures (T_{im} , T_{pm} , and T_{em})

(9) Crystallization temperatures (T_{ic} , T_{pc} , and T_{ec})

(10) Glass transition temperatures (T_{ig} , T_{mg} , and T_{eg})

(11) Year, month, and day of test

(12) Other items required